Effect of Cathodic Polarization of n-TiO_2 Thin Films on Their Photoresponse towards Water Splitting Reactions

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Cathodic reduction of Titanium oxide (n-TiO_2) thin films was investigated as an alternative approach to customary hydrogen modification of n-TiO_2 under hydrogen gas stream at high temperature. Hydrogen modification of n-TiO_2 was carried out electrochemically under cathodic polarization. The photo-response of the electrochemically hydrogen modified n-TiO_2 (HM-n-TiO_2) exhibited a four-fold enhancement in their photoresponse compared to n-TiO_2 during water splitting under solar simulated light. The photoactivity of HM-n-TiO_2 suffers a substantial decrease after heat-treatment at 200°C, remarkably the photoactivity of these samples was fully repaired after re-hydrogenation under similar conditions. The electrodes were characterized using electrochemical and spectroscopic techniques.
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Solar water splitting on the surface of semiconductors offers a green process for hydrogen generation. Due to its chemical stability in basic electrolytes numerous studies have been conducted on n-TiO_2 as a catalyst of choice for water splitting,[1–9] however, n-TiO_2 is a poor photons absorber of the solar spectrum (due to their intrinsic bandgap, both anatase (3.2 eV) and rutile (3 eV) absorb only the UV light that accounts for about 3% of the solar radiation.).[8] One popular approach to address the sluggish photoresponse of n-TiO_2 is to dope the semiconductor with extraneous chemical elements and thus decrease its photo threshold energy.[4,5,10–13] Transition metals as dopands were intensively investigated. Since this effort showed limited success scientists shifted the interest to nonmetallic elements such as carbon,[5,6] nitrogen,[4,7] sulfur,[8] and hydrogen.[14–16] Hydrogen modification of n-TiO_2 was mainly achieved by heat-treatment of n-TiO_2 powder under a reduced atmosphere of hydrogen gas.[14–16] Upon incorporation of hydrogen within the structure of n-TiO_2 particles the native white color of n-TiO_2 was blackened and the spectral response of hydrogen doped n-TiO_2 was found to shift to the visible part of the incident light used.[14–16]

In this study we investigate the electrochemical hydrogenation of the pristine n-TiO_2 thin film during hydrogen evolution on its surface. This is a simple one step technique that consists of cathodic polarization of n-TiO_2 thin films in alkaline electrolyte under dark conditions. During this process hydrogen evolves on the surface of the electrode and consequently the later may undergo hydrogen adsorption on the surface or protons intercalation within the lattice of the semiconductor to compensate for the negative charges at the cathode.[18] We have previously shown that the electrochemical reduction (hydrogenation) of n-TiO_2 thin films in alkaline electrolyte enhances their photocurrent during water splitting compared to the pristine n-TiO_2 thin film electrodes.[17,19] This finding prompted us to investigate the long-term stability of the photocurrent generated by the cathodically polarized n-TiO_2. In particular, we focused in determining whether HM-n-TiO_2 could remain photoactive in its reduced form for a longer time. Moreover, in this study the effect of heat-treatment of HM-n-TiO_2 on its photoactivity was also investigated. In addition, XPS data were collected to determine any reduction induced change in valence band of HM-n-TiO_2.

Experimental

Ti metal sheets of 0.25 mm thick (Alfa Co.) were cut and cleaned as reported earlier.[17] The Ti sheets were thermally oxidized to n-TiO_2 in a tubular electric furnace at 825°C for 16 minutes. The n-TiO_2 thin films were then reduced by applying a negative voltage of −1.6 V vs SCE in a custom made single compartment three electrodes electrochemical cell, where, n-TiO_2, Pt, and saturated calomel electrode (SCE) were used as the working, counter, and reference electrodes, respectively. The electrochemical reduction or hydrogen modification of n-TiO_2 was carried out in 2.5 M KOH electrolyte solution under dark conditions for 6 minutes.

Linear sweep voltammetry (LSV) was used to study the electrochemical behavior of the photoelectrodes, HM-n-TiO_2, thin films using a PAR (VersaSTAT 3) scanning potentiostat at a scan rate of 50 mV s^{-1}. These experiments were performed in the same electrochemical cell and electrolyte as mentioned above under dark and under solar simulated light illumination (0.1 W cm^{-2}). The working HM-n-TiO_2 electrodes were placed at a distance of 8 inches from the light source. The photocurrent density (J_{photo}) was obtained by subtracting the dark current density (J_{dark}) from the current density under illumination, J_{total} ($J_{photo} = J_{total} - J_{dark}$). A solar simulator (Thermo Oriel model 81192) equipped with 1000 W Xenon lamp and a global AM 1.5 filter was used as a light source throughout this study. The light intensity was measured using Si detector (Model 10DP/SB). The wavelength dependent (monochromatic) photocurrent density was measured using the Monochromator, model 77250 of Spectra Physics. All potentials were referenced to the saturated calomel reference electrode (SCE).

Surface morphology of the synthesized thin film oxides was characterized using Scanning Electron Microscopy (SEM), and was performed on a high-resolution Hitachi S-3400 SEM. The Hitachi S-3400 SEM equipped with a Bruker Quantax energy dispersive spectrometer was also used for energy dispersive spectroscopic (EDS) analysis. EDS spectra were collected at accelerating voltage of 15 kV and a working distance of 10 mm

Crystallographic data were collected from X-ray diffraction (XRD) using PANalytical X'Pert-Pro MPD with 45 kV Cu Kα radiation source (λ = 1.541 Å). Scans were collected from 20 to 70 degrees 2θ at a continuous scan rate. Any possible change in the valence band induced by the hydrogenation of n-TiO_2 was examined by X-ray photoelectron spectroscopy (XPS). Measurements were carried out for both n-TiO_2 and HM-n-TiO_2 using a Leybold LHS-10 spectrometer with MgKα (1253.6 eV) X-ray source at a pass energy of 100 eV. The pressure in the analysis chamber was typically 2×10^{-8} Torr.

Results and Discussion

The photoresponse of the photoanodes, HM-n-TiO_2, was evaluated by measuring the rate of oxygen evolution reaction (OER) in terms of the anodic photocurrent density, J_p (mA cm^{-2}) during water

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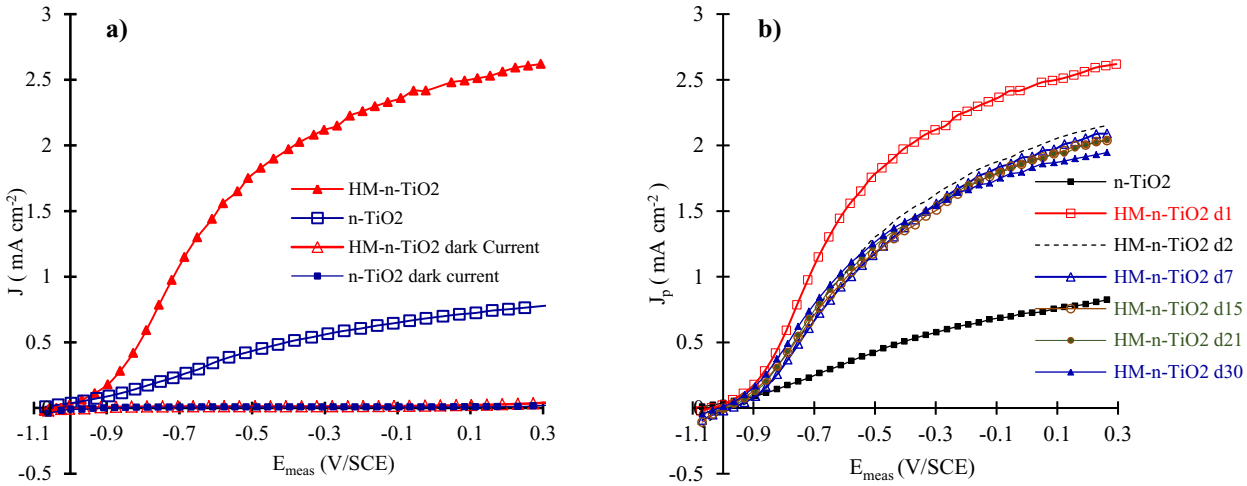

Figure 1. a) Photocurrent and dark current densities vs measured potential, E_{meas} (V/SCE) plots for *n*-TiO_2 and HM-*n*-TiO_2 thin film electrodes in 2.5 M KOH electrolyte and under solar simulated light (0.1 W cm^{-2}), b) Photocurrent density, J_p, vs measured potential, E_{meas} (V/SCE) plots for *n*-TiO_2 and HM-*n*-TiO_2 thin films in 2.5 M KOH electrolyte and under solar simulated light (0.1 W cm^{-2}) in day 1 to day 30.

splitting reaction. Figure 1a shows the dependency of photo current and dark current densities J, as a function of measured potential (E_{meas} vs SCE) for *n*-TiO_2 and hydrogen modified HM-*n*-TiO_2. No noticeable difference in dark current was observed before and after cathodic polarization of *n*-TiO_2 as is shown in Figure 1a. It is observed in Figure 1a that at −0.4 V/SCE the photocurrent density enhanced to 1.97 mA cm^{-2} for HM-*n*-TiO_2 compared to 0.5 mA cm^{-2} for undoped *n*-TiO_2. This four-fold enhancement in the photocurrent density can be attributed to non-stoichiometric nature of the partially reduced *n*-TiO_2 by hydrogen incorporation at the surface and in the lattice of *n*-TiO_2 during the cathodic polarization.

Photocurrent vs potential measurements at HM-*n*-TiO_2 electrode were carried out once for every day for 30 days. Initially, the photoactivity of HM-*n*-TiO_2 decreased after the first day (HM-*n*-TiO_2 d1) then exhibited a substantial steadiness for the following 29 days as shown in Fig. 1b. Prior to each measurement, HM-*n*-TiO_2 was rinsed with DI-water and then dried at room temperature under ambient atmosphere. Because hydrogen tends to be attracted to dangling bonds,[15] we believe that the initial drop in the photoactivity could be due to the loss of all or some of the hydrogen attached to the surface of the HM-*n*-TiO_2 semiconductor.

At the cathodic potential of −1.6 V vs SCE in 2.5 M KOH solution, the only reaction expected at the electrode surface is the hydrogen evolution reaction (HER). According to Lemon and hupp[18] besides molecular hydrogen formation during reduction some of the protons are incorporated within the structure of *n*-TiO_2 to compensate for the negative charge at the cathode. Ultimately proton insertion (as impurities) would help to increase the nonstoicheometry/defect in the semiconductor structure which may lead to the formation of mid-gap states where electrons could be excited from either the valence band or the newly created states to the conduction band and thereby, enhanced the photoresponse.

Fig. 2a shows the photocurrent potential dependency of HM-*n*-TiO_2 and its heat treated samples at various temperatures: 100°C, 150°C and 200°C for an hour. It is observed that the photocurrent density decreased significantly for samples heated at 200°C. This indicates that the most of the incorporated or adsorbed hydrogen atoms were removed during heat-treatment at this temperature. Interestingly, the photoactivity of heat treated samples was restored (see Fig. 2b) after re-reducing them under the same cathodic polarization condition. We believe that this finding supports to a great extent the fact that part of the hydrogen was adsorbed at the surface of the electrode.

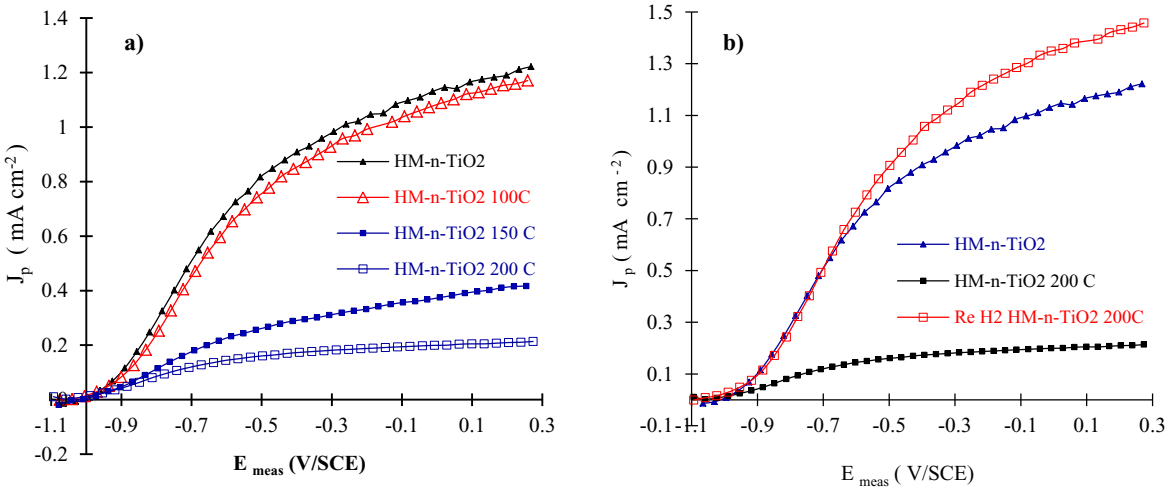

Figure 2. a) Photocurrent density, J_p vs measured potential, E_{meas} (V/SCE) plots for HM-*n*-TiO_2 and for heat treated HM-*n*-TiO_2 thin film electrodes at 100°C, 150°C and 200°C, b) Photocurrent density of HM-*n*-TiO_2, the heat treated HM-*n*-TiO_2 at 200°C (HM-*n*-TiO_2 200°C) and the re-hydrogenated HM-*n*-TiO_2 (Re H_2 HM-*n*-TiO_2 200°C) thin film electrodes as a function of the applied potential.

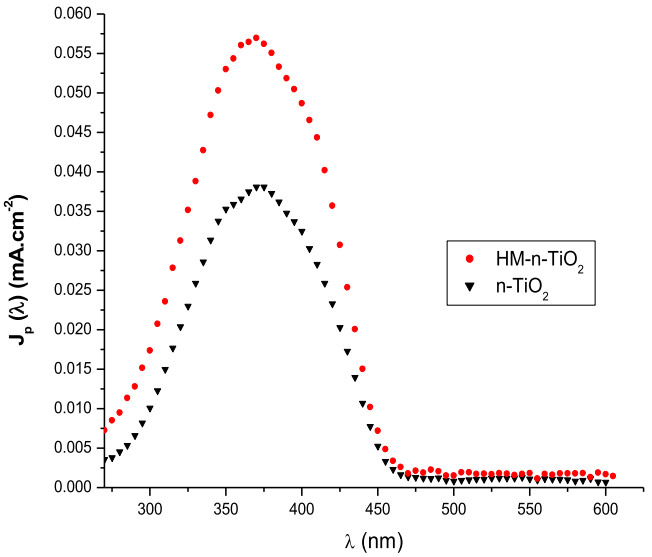

Figure 3. Monochromatic photocurrent density, $j_p(\lambda)$, as a function of wavelength of light, λ (nm), for unmodified *n*-TiO_2 and HM-*n*-TiO_2 .The monochromatic photocurrent measurements were performed under monochromatic light intensity of 0.1 W cm^{-2} from a global AM 1.5 solar simulator and 2.5 M KOH as electrolyte. The measured potential used was set at 0.2 V vs SCE.

Surface morphology of *n*-TiO_2 thin films was investigated using scanning electron microscopy (SEM) before and after hydrogenation and no observable of differences were observed. It should be also noted that H atom cannot be detected by EDS. Furthermore, presence of K^+ was not observed in the EDS spectra of HM-*n*-TiO_2 indicating the absence of its intercalation.

The cathodic polarization may have changed the electronic properties of *n*-TiO_2 and consequently its photoresponse. The higher photocurrent density of HM-*n*-TiO_2 at each wavelength compared to that of *n*-TiO_2 can be attributed to enhancement of its electronic conductivity during cathodic polarization (see Fig. 3).

X-ray diffraction spectroscopy (XRD) was used to investigate the structure of *n*-TiO_2 thin films before and after hydrogenation. After hydrogenation, the HM-*n*-TiO_2 thin film XRD pattern exhibits the same crystalline phase consists mainly on rutile phase with some peaks

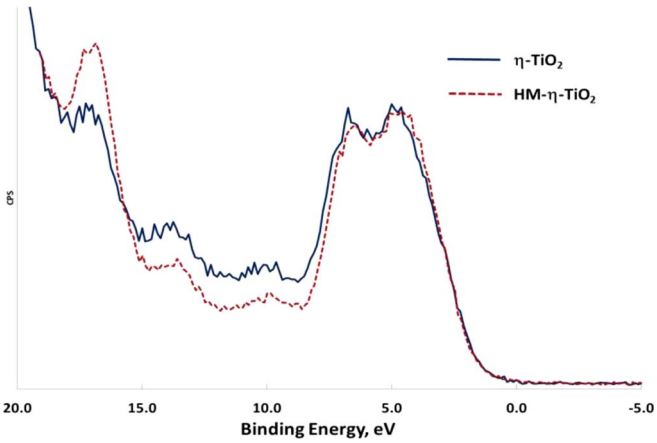

Figure 4. Valence-band X-ray photoelectron spectroscopic (XPS) spectra for regular *n*-TiO_2 and HM-*n*-TiO_2.

belonging to the anatase phase. It should be mentioned that reduction or hydrogenation of *n*-TiO_2 did not change its crystalline structure which is consistent with other studies.[15,16] Therefore, the incorporation of hydrogen could be either limited to the surface of the electrode or a possible charge compensating cations (protons) intercalation into the lattice of *n*-TiO_2. The intercalation of hydrogen into the lattice of *n*-TiO_2 was suggested by Lemon et al[18] who confirmed proton insertion with the use of Quartz Crystal Microbalance analysis.

The density of states (DOS) valence band of *n*-TiO_2 and HM-*n*-TiO_2 were measured by valence-band X-ray photoelectron spectroscopy (XPS) (see Fig. 4). Both sample display similar valence band density of state (found from the binding energy threshold in Fig. 4). The similar valence band edges for both samples is also consistent with similar value of bandgap energy of about 2.7 eV for both samples as is observed from the threshold of monochromatic photocurrent density at 460 nm (2.7 eV) as shown in Figure 3. The XPS valence band data is slightly different from what was reported by Chen et al.[15,16] It should be noted that in the case of *n*-TiO_2 particles hydrogenation was carried out under hydrogen flow at high temperature (600°C[14] and 200°C[15]).

Conclusions

We have demonstrated a simple approach to incorporate hydrogen into *n*-TiO_2 thin films electrochemically by cathodic polarization at room temperature. The photoresponse of the electrochemically synthesize hydrogen modified titanium oxide, HM-*n*-TiO_2, toward water splitting enhanced by four-fold compared to a regular *n*-TiO_2. Also, it was found that the effect of hydrogen incorporation in *n*-TiO_2 lattice on the rate of photoelectrochemical water splitting can be tuned by thermal treatment of HM-*n*-TiO_2 at different temperatures. It's worth noting that the photoactivity of HM-*n*-TiO_2 samples decreased after heat-treatment at 200°C, however their photoactivity can be easily restored after re-hydrogenation of the same samples under the similar experimental conditions. To a certain extent this support the fact that part of the hydrogen was adsorbed at the surface of the electrode.

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